

Attorney's Docket Number: 2002JP309

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Yasushi Akiyama

Serial No.: 10/518,105

Group Art. Unit: 1795

Filed: December 10, 2004

Examiner: Chanceity N. Robinson

For: Process for preventing development defect and composition for use in the same.

Commissioner for Patents

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DECLARATION UNDER 37 C. F. R. § 1.132

I, Yasushi AKIYAMA, a Japanese citizen, residing in Kakegawa-shi, Japan, declare as follows:

I received a Bachelor of Science degree from Yokohama City University in March, 1999 and a Master of Science degree in organic chemistry from Yokohama City University in March, 2001. I had been employed by Clariant (Japan) K.K. as a research & development engineer from April, 2001 to October, 2004, and then, I have been employed by AZ Electronic Materials (Japan) K.K. as a research & development engineer since October, 2004. I have been involved in research and development work relating to photoresists and ancillary chemicals since 2001.

I have been named as an inventor on at least 2 US pending Patents and 4 Japanese pending patent applications. I am an applicant in the above-mentioned patent application and an inventor of the invention claimed therein. I am familiar with the Takano reference which was used in the rejection of the claims in the above application.

The following experiments were performed by me or under my direction and control.

### EXPERIMENTAL REPORT

#### Test

##### Example 1

1.0 parts by weight of polyacrylic acid (PAA) having weight average molecular weight of 3,000 as determined by polystyrene standards as a water-soluble polymer, 1.65 parts by weight of perfluoro-octylic acid ( $C_7F_{15}COOH$ ) (PFOA) as an organic acid, 0.33 parts by weight of tetramethylammonium hydroxide (TMAH) (equivalent ratio (mole) of organic acid and base is 1:0.9) as a base were mixed up. Pure water was added thereto to make the total amount 100 parts by weight. Then, the solution was solved homogeneously at room temperature, and filtered with a 0.1  $\mu m$ -filter to obtain the composition for preventing development-defects.

On the other hand, a positive-working photoresist comprising acetal type polymer manufactured by Clariant (Japan) K.K. (AZ DX3301 P, 'AZ' is a registered trade mark.) was applied on an 8 inches silicon wafer by a spin coater made by Tokyo Electron Co. (Mark 8). It was pre-baked on a hot plate at 90°C for 90 seconds to form a photoresist film of 480 nm in thickness on a silicon wafer. The film thickness was measured by film thickness measuring equipment SM300 manufactured by Prometric Co.

Subsequently the above described composition for preventing development-defects was applied on the photoresist film by using the same spin coater as the above. It was then pre-baked on a hot plate at 90°C for 60 seconds to form a film for preventing development-defects on a photoresist film of 450 Å in thickness. Next, exposure to light was conducted by using KrF reduced projection exposure equipment, FPA 3000-EX5, PEB was conducted on a hot plate at 110°C for 60 seconds. Using alkali developer, AZ 300MIF Developer (2.38 weight % tetramethylammonium hydroxide aqueous solution; 'AZ' is a registered trade mark.) as a developer, it was paddle-developed on the condition of 23°C for 1 minute, to obtain a resist pattern having 1:1 line and space width. And also the film thickness after development was measured using the same equipment as one described above. The amount of film reduction in thickness was obtained by deducting the film thickness after development from one before development. The cross sectional form of the formed resist pattern was observed by Scanning Electronic Microscope (SEM). Observation result of the cross-sectional form of the resist pattern and the amount of film reduction in thickness are shown in the Table-1 and Graph-1 described below.

#### Examples 2 to 6

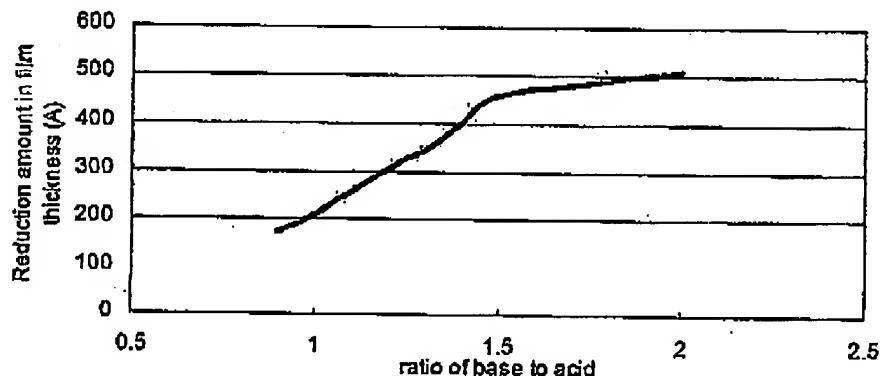
The same manner was taken as in Example-1 except that the equivalent (mole) ratios of base were made as described in Table-1. The results are shown in Table-1 and Graph-1 below.

#### Example 1 and 2 in the present specification

The condition and manner were same as described in Example-1 except that the equivalent (mole) ratios of base were made as described in Table-1. The results are shown in Table-1 and Graph-1 below.

Table-1. PAA(polymer), TMAH(base), PFOA(acid)

	Acid	Base	Reduction amount in film thickness (Å)	Pattern Profile
Example 1	1	0.9	171	T-top (corrected from previous Declaration)
Example 2	1	1	210	almost rectangular
Example 3	1	1.3	344	rectangular
Example 4	1	1.4	401	rectangular
Example 5	1	1.5	458	almost rectangular
Example 6	1	2	510	almost rectangular
Example 1 in the specification	1	1.04	230	almost rectangular
Example 2 in the specification	1	1.25	329	rectangular

Graph-1. PAA(polymer), TMAH(base), PFOA(acid)**Example 7**

1.0 parts by weight of polyacrylic acid having weight average molecular weight of 3,000 as determined by polystyrene standards as a water-soluble polymer, 1.8 parts by weight of perfluoro-octylic acid ( $C_7F_{15}COOH$ ) (PFOA) as an organic acid, 0.27 parts by weight of monoethanolamine (MEA) (equivalent ratio

(mole) of organic acid and base is 1:1) as a base were mixed up. Pure water was added thereto to make the total amount 100 parts by weight. Then, the solution was solved homogeneously at room temperature, and filtered with a 0.1  $\mu\text{m}$ -filter to obtain the composition for preventing development-defects.

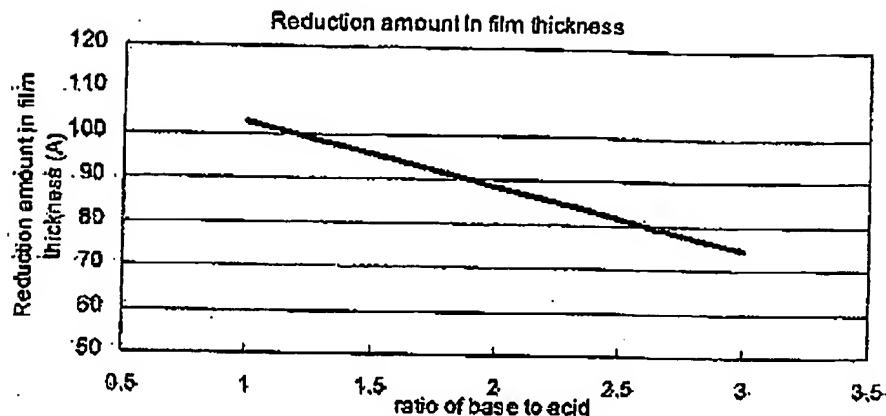
In the same manner as in above described Example 1, the silicon wafer on which a positive-working chemically amplified photoresist was applied was prepared. Then, coating above described composition for preventing development-defects on the photoresist film, exposure to light, PEB and development were conducted in the same manner as in Example 1 and a pattern form of resist cross section was observed and the amount of reduction in film thickness was measured. The result is shown in Table-2 and Graph-2 described below.

#### Examples 8 and 9

The same manner was taken as in Example 7 except that the equivalent (mole) ratios of base were made as described in Table-2. The results are shown in Table-2 and Graph-2 below.

Table-2. PAA(polymer), MEA(base), PFOA(acid)

	Acid	Base	Reduction amount in film thickness ( $\text{\AA}$ )	Pattern Profile
Example 7	1	1	102.8	T-top
Example 8	1	2	88.5	T-top
Example 9	1	3	74.6	T-top



Graph-2. PAA(polymer), MEA(base), PFOA(acid)

Example 10 (based on Example 1 of Takano JP 2002-006514)

1.0 parts by weight of Polyvinylpyrrolidone (PVP) having weight average molecular weight of 45000 as determined by polystyrene standards as a water-soluble polymer, 1.8 parts by weight of perfluorooctanesulfonic acid ( $C_8F_{17}SO_3H$ ) as an organic acid, 0.22 parts by weight of monoethanolamine (MEA) (equivalent ratio (mole) of organic acid and base is 1:1) as a base were mixed up. Pure water was added thereto to make the total amount 100 parts by weight. Then, the solution was solved homogeneously at room temperature, and filtered with a 0.1  $\mu$ m-filter to obtain the composition for preventing development defects. In the same manner as in above described Example 1, the silicon wafer on which a positive-working chemically amplified photoresist was applied was prepared. Then, coating above described composition for preventing development defects on the photoresist film, exposure to light, PEB and development were conducted in the same manner as in Example 1 and a pattern form of resist cross section was observed and the amount of reduction in film thickness was measured. The result is shown in Table-3 and Graph-3 described below.

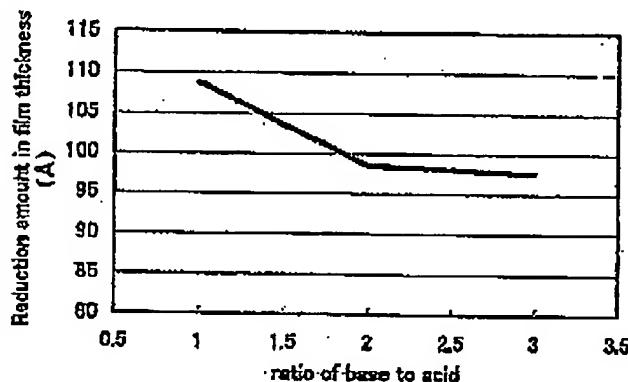
Example 11 to 12

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The same manner was taken as in Example 10 except that the equivalent (mole) ratios of base were made as described in Table-3. The results are shown in Table-3 and Graph-3 below.

Table-3. PVP(polymer), MEA(base), PFOS(acid)

	Acid	Base	Reduction amount in film thickness (Å)	Pattern Profile
Example 10	1	1	108.8	T-top
Example 11	1	2	98.5	T-top
Example 12	1	3	97.5	T-top



Graph-3. PVP(polymer), MEA(base), PFOS(acid)

## Results

In the present invention, base is restricted to TMAH, increase of the film loss is achieved when the ratio of base to acid is larger than 1, as shown in the above Graph-1. Also, the data in Table-1 show perfect or virtually perfect pattern profile (rectangular or almost rectangular). However, pattern profile is poor (T-top) when the ratio of base to acid is smaller than 1 (Example 1).

Table -1 shows the results on lower-end point of 1:1:1.04 and ratio of between 1:1 and 1:1.3 from the specification.

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When MEA is selected for base, decrease of the film loss is observed in the case of the ratio of base to acid is larger than 1, as shown in the above Graphs-2. The maximum film loss is achieved when the ratio of base to acid is 1 but the reduction of film thickness is 102.8 Å. The data in Table- 2 shows that pattern profile is poor (T-top). Comparison between Graph-1 and Graph-2 indicates that specific base (TMAH) is effective.

Adopting the polymer, base and acid described in the prior art, mixing ratio of the base to acid was adjusted. As shown in the above Graph-3, decrease of the film loss is observed in the case of the ratio of base to acid is larger than 1. The maximum film loss is achieved when the ratio of base to acid is 1 but the reduction of film thickness is 108.8 Å. Increase of the film loss cannot be obtained by just adjusting mixing ratio of the base to acid when the ratio of base to acid is larger than 1. Also, the data in Table- 3 shows that pattern profile is poor (T-top).

Taking into consideration of these results and Examples in the specification, the present invention cannot be anticipated from the prior art.

I declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true, and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both (18 U.S.C. 1001) and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

8th Oct, 2009

(date)

Yasushi Akiyama

Yasushi Akiyama